



Eurometaux
Environmental Classification Workshop
Setting an ecotox reference value

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And others...

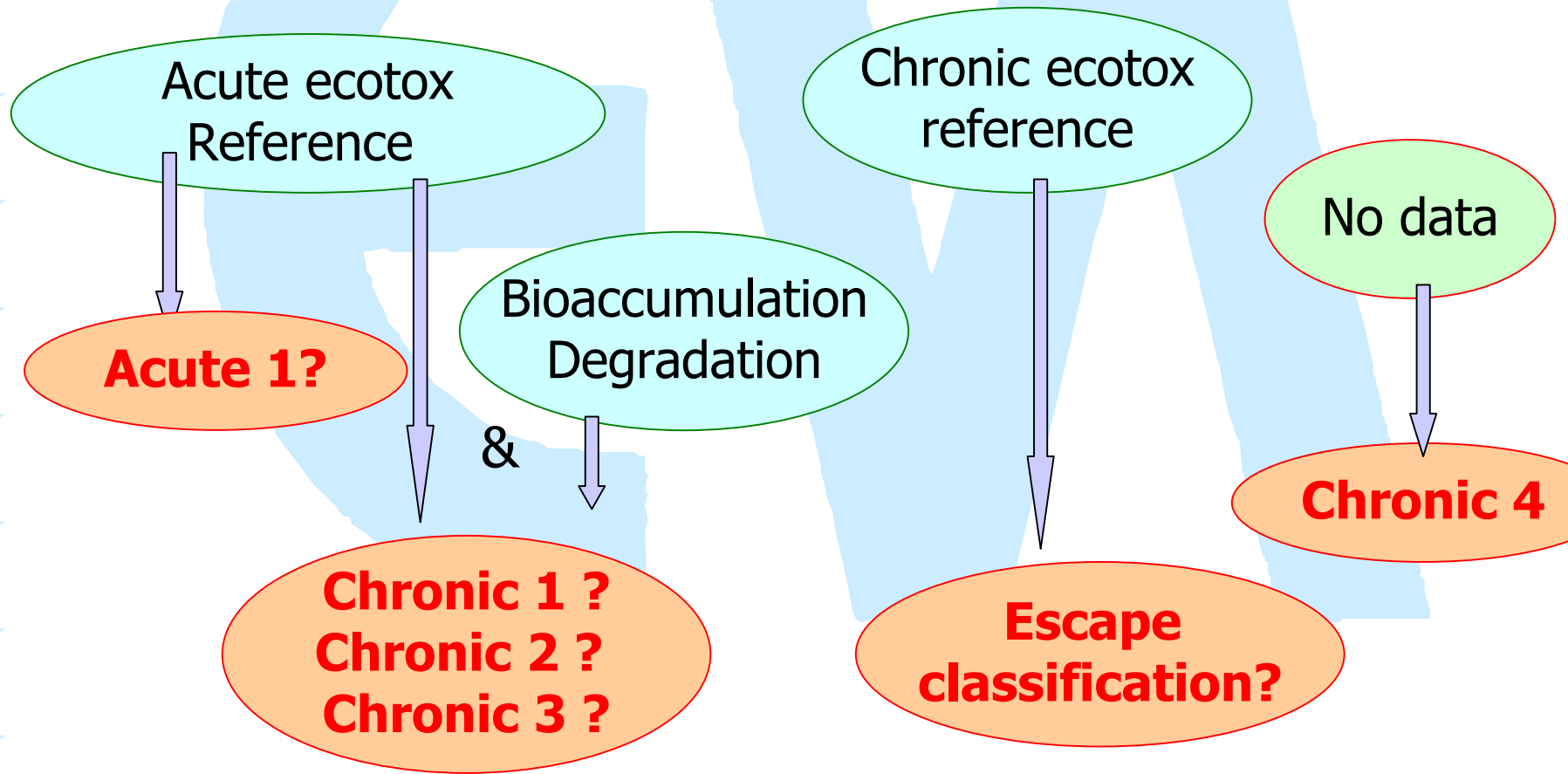
EU Environmental Classification

- Dangerous substance directive : 67/548/EEC
- Dangerous preparation directive : 88/379/EEC
- **CLP REGULATION : 1272/2008**

General Principle of the classification

The CLP REGULATION : 1272/2008

= essentially a chronic classification system



Metal risk assessment guidance (MERAG)

→ MERAG

- ✓ Classification and Labelling fact sheet

→ Objective MERAG

- ✓ Aimed at the consolidation of the technical and scientific knowledge on metals which advanced significantly over the last couple of years.

<http://www.euras.be/merag>

→ Incorporation of new concepts in RIP 3.6

How to do Hazard Classification



Classification of soluble metal compounds

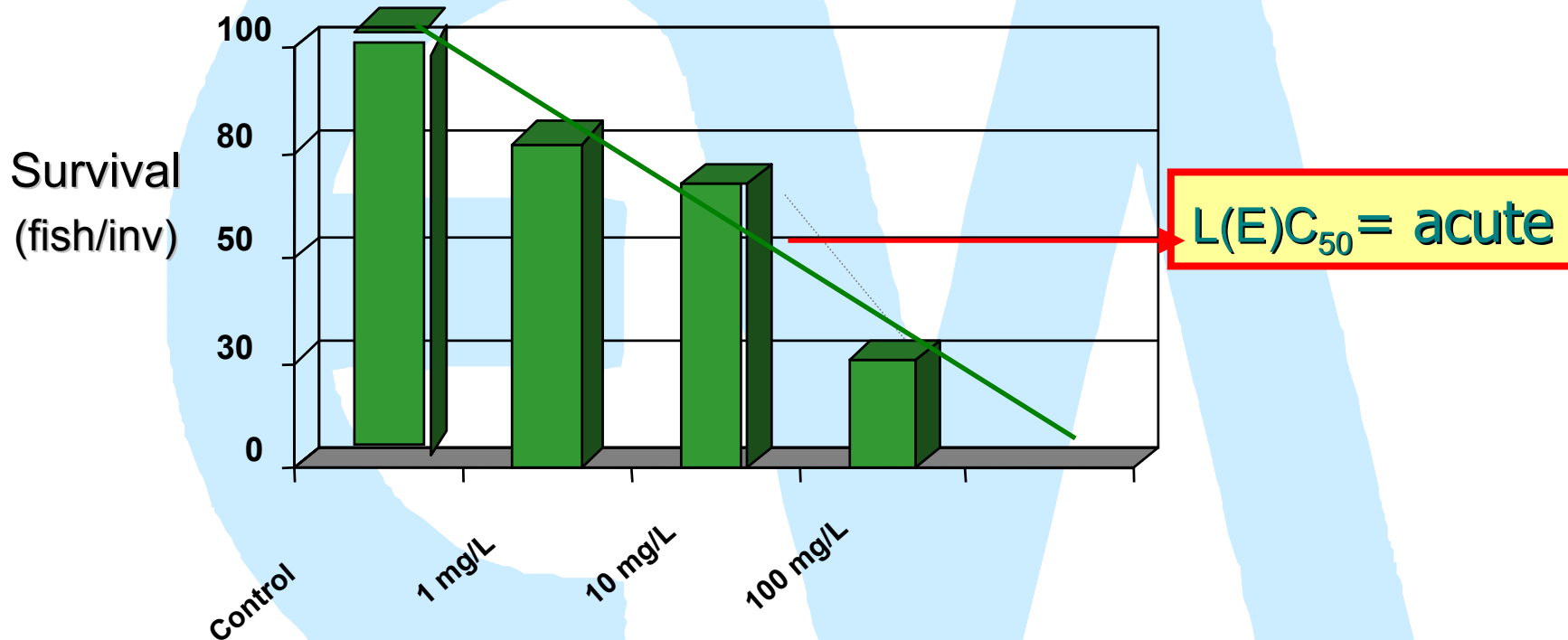
- Derivation of Acute Ecotoxicity Reference value (A-ERV)
- Derivation of Chronic Ecotoxicity Reference value (C- ERV)
 - ✓ Data selection
 - ✓ Data aggregation
 - ✓ Derivation of acute and chronic ERV
- **Assessing «Biaccumulation potential»**
- **Assessing «Degradation»**

M. Vangheluwe : Classification strategy for metals and metal/compounds

- ✓ Soluble form
- ✓ Sparingly/insoluble soluble forms

Deriving ecotoxicity values - principles

Dose response and Endpoints :



LC50 = Concentration causing mortality to 50 the tested organisms

EC50 = Concentration causing an effect to 50 the tested organisms
or causing an effect of 50%

NOEC= highest Concentration causing no effect

Deriving ecotoxicity values – Test set-up

Test set-up - OECD 201,202, 203, 210, 211 protocols (RIP 3.6)

| Acute Test protocols(EC50) | Chronic Test protocols (NOEC) |
|-----------------------------|--------------------------------------|
| -Fish mortality (96 hrs) | -Fish 30 days, early life stage test |
| -Invertebrates (48 hrs) | -Invertebrates (28days) |
| -Algae growth rate (72 hrs) | -Algae growth rate (72 hrs) |
| -Lemna (14 days) | |

Test species : preferable see protocols – freshwater & seawater

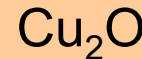
Test Substance : Assess ecotoxicity of the release of metal ion (Me²⁺...)

Soluble compounds



Ref Ecotox

Sparingly soluble compounds



Ref Ecotox + T/D

Metal



Deriving ecotoxicity values – Data selection

The best quality data & most sensitive as basis for the classification « **Quality criteria - Data hierarchie** »

1. Type of test (standard tests (e.g. OECD) preferred for classification)
 - *Concentration-effect relationship : effect between 0 & 100%*
 - *Validity requirements : control requirements, statistics, test concentration interval (\leq factor of 2); evidence on test concentration (measurements)*
 - *Description of test method (endpoints, physico-chemical test conditions, bioavailability parameters, culture conditions)*
2. Standard species preferred but non-standard species can be used in case of equivalent endpoints
3. Relevancy of test medium (natural & artificial media, conditions related to transformation/dissolution media for classification)
4. Relevancy of test substance (solubility, impurities) : tests on soluble metal compounds

Classification for soluble metal compounds

→ Classification :

Reference ecotoxicity – soluble compound
expressed as $\mu\text{g Me/L}$

&

Molecular weight correction

Derivation ecotoxicity reference value soluble metal compounds

Acute & chronic ecotoxicity data
compilation (algae, invertebrates, fish)



Quality screening (quality criteria)



Aggregation of high quality
toxicity data – (ug Me/L)



Species mean values ($\mu\text{g Me/L}$)
>4 data-points/species



**Use lowest species mean
acute/chronic values as
reference ecotoxicity points
for the Classification**

No data aggregation
across species!!!



M wt correction from e.g. $\mu\text{g Cu/L}$ to $\mu\text{g CuSO}_4/\text{L}$

Sparingly soluble metal species & metals

→ Classification :

Reference ecotoxicity – soluble compound
expressed as $\mu\text{g Me/L}$

&

Transformation Dissolution at pH 6,7 8

Derivation ecotoxicity reference value metals and sparingly soluble compounds

Acute & chronic ecotoxicity data
compilation (algae, invertebrates, fish)



Quality screening (quality criteria)



Aggregation of high
quality toxicity data



Species mean
values
>4 data-
points/species



**Bioavailability
normalization**

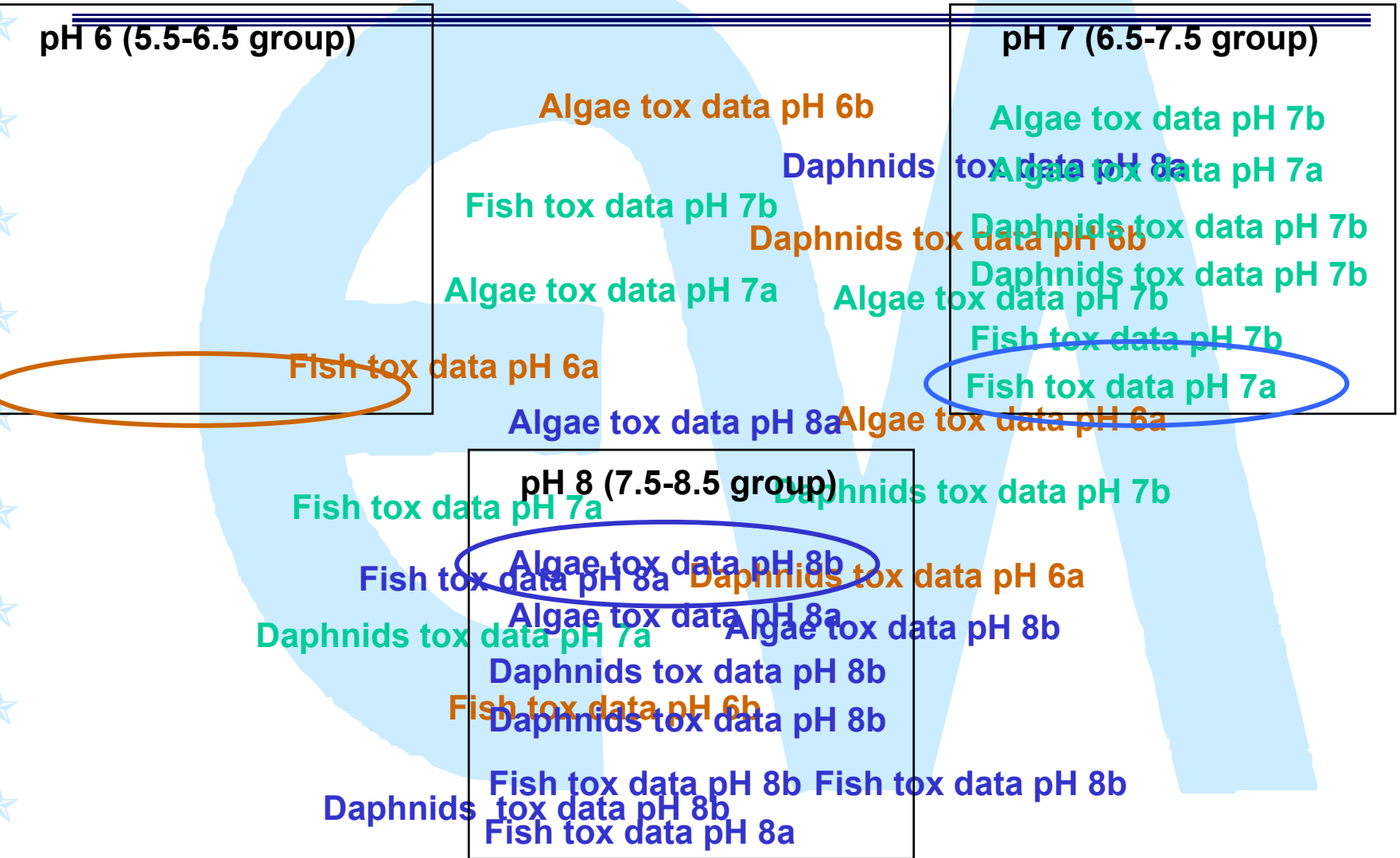


Derivation of reference values for different pHs ($\mu\text{g Me/L}$)



M wt correction &/or T/D

Derivation of ERV-aggregation-lowest value



Derivation of ERV-lowest value-bioavailability normalization

pH 6 (5.5-6.5 group)

Algae tox data pH 8b

Algae tox data pH 8a

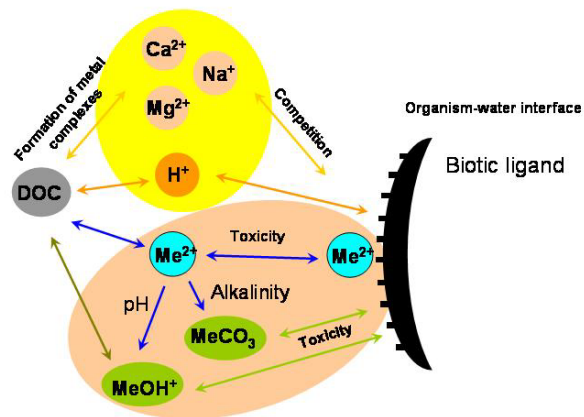
Daphnids tox data pH 8b

Daphnids tox data pH 8a

Fish tox data pH 8b

Fish tox data pH 8a

Bioavailability normalization



pH 7 (6.5-7.5 group)

Algae tox data pH 7b

Algae tox data pH 7a

Daphnids tox data pH 7b

Daphnids tox data pH 7b

Fish tox data pH 7b

Fish tox data pH 7a

pH 8 (7.5-8.5 group)

Algae tox data pH x

Algae tox data pH x

Daphnids tox data pH x

Daphnids tox data pH x

Fish tox data pH x

Fish tox data pH x

Algae tox data pH ~~8~~b

Algae tox data pH ~~8~~a

Daphnids tox data pH ~~8~~b

Daphnids tox data pH ~~8~~b

Fish tox data pH ~~8~~b

Fish tox data pH ~~8~~a

Algae tox data pH x

Algae tox data pH x

Daphnids tox data pH x

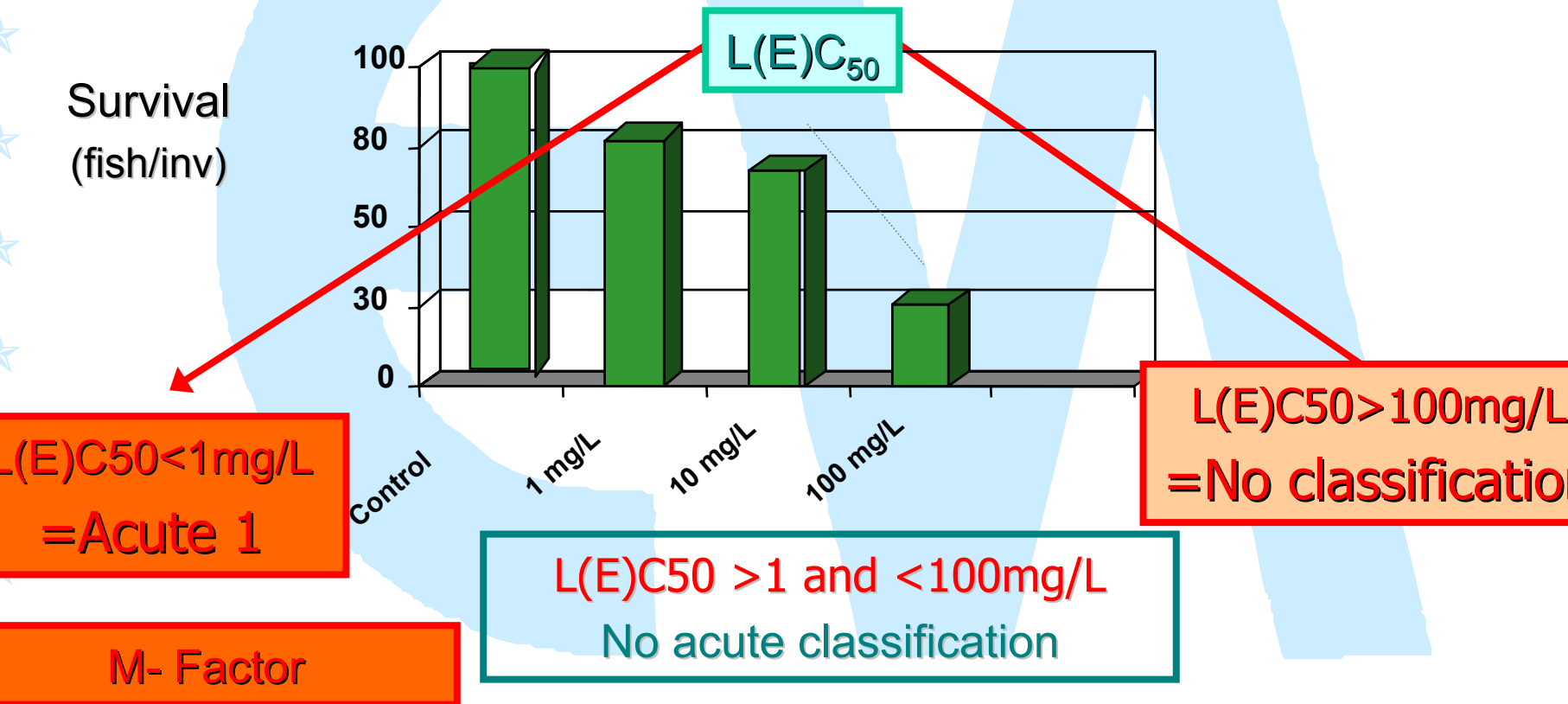
Daphnids tox data pH x

Fish tox data pH x

Fish tox data pH 7a

Reference ecotoxicity vs acute classification

Data interpretation – Acute Endpoint vs classification categories



Classification example

Cu data-selection - lowest value vs species mean

| Test organism | L(E)C ₅₀ (µg/l) | | | |
|-----------------------|----------------------------|-----------------|------------------|---------|
| | pH: 5.5-6.5 | pH: >6.5-7.5 | pH: >7.5- 8.5 | All pHs |
| Algae | | | | |
| <i>R. subcapitata</i> | | | | |
| n | 2 | 3 | 12 | 17 |
| Min. | 152.0 | 32.0 | 12.9 | 12.9 |
| Max. | 194.0 | 163.1 | 245.3 | 245.3 |
| Geometric mean | 171.7 | 76.0 | 61.8 | 72.3 |

Classification examples

Copper data-selection – lowest species mean

| pH range | Non-normalised L(E)C₅₀ (µg/l) |
|-----------------|---|
| pH 5.5-6.5 | 29.2 |
| pH >6.5-7.5 | 47.3 |
| pH >7.5-8.5 | 29.8 |

Ecotoxicity reference value : 29 µg Cu/L

Classification examples

Read across from soluble metal species

Ecotoxicity of soluble metals species – read-across

= Molecular weight correction & T/D

Copper example - Reference ecotox acute : 29 $\mu\text{g Cu}^{2+} / \text{L}$

| Substance | Mol. wt | T/D ratio - 7 days mg Me ⁺⁺ /mg MC | Final acute reference $\mu\text{g Cu/L}$ | Derivation acute reference | Classification |
|-------------------------|---------|--|---|--------------------------------|-------------------|
| Copper ions | 63.55 | | 29 | Ecotox tests soluble compounds | |
| Copper sulphate pentahy | 213.6 | | 98 | Acute ref copper ions & Mol wt | Acute 1, M=10 |
| Copper (I) oxide | 159.6 | 0.05 | 73 | acute ref + 7 days T./D | Acute 1, M=10 |
| Copper powder | 63.55 | 0.088 | 332 | acute ref + 7 days T./D | Acute 1 |
| Copper massive | 63.55 | $<0.77 \cdot 10^{-3}$ | 37922 | acute ref + 7 days T./D | No classification |

Presentation Marnix Vangheluwe
+ alloys presentation (abrasion issue)

Reference ecotoxicity vs chronic classification

Data interpretation – chronic classification categories

L(E)C50 < 1 mg/L

=Acute 1



Chronic 1?

L(E)C50 > 1 and < 10 mg/L



Chronic : 2-3?

L(E)C50 : > 10 -> 100 mg/L



Chronic : 2-3?

- Biodegradation?
- Bioaccumulation?
- Chronic NOEC < 1 mg/L?

Biodegradation/removal from water column

Biodegradation = removal from the water column

1. Speciation/precipitation

= Solubilization of 1 mg/L, Settle for 28 days at relevant pHs (6-8.5)

IF soluble Me concentration < chronic reference NOEC

→ = metal is rapidly removed from the water column Ex : Al, Fe,

2. Precipitation and partitioning

= Test concentration between NOEC & EC50; natural water (suspended solids concentration <15 mg/L); pH 6-8.5; Settle for 28 days

- IF removal from the water column >70%

and

- IF Me-OC stability constant < Me Sulphide stability constant

→ = metal is rapidly removed from the water column

BIOACCUMULATION

1. Essential metals:

= not applicable

2. Non Essential metals:

- recognition of variable BCF
 - BCF to be determined at/around EC50 value of the reference species (invertebrates/fish)
 - Whole body measurements
 - Geometric mean value if > 4 equivalent data-points (same species/same endpoint)
- = if $BCF < 500$: no potential for bioaccumulation

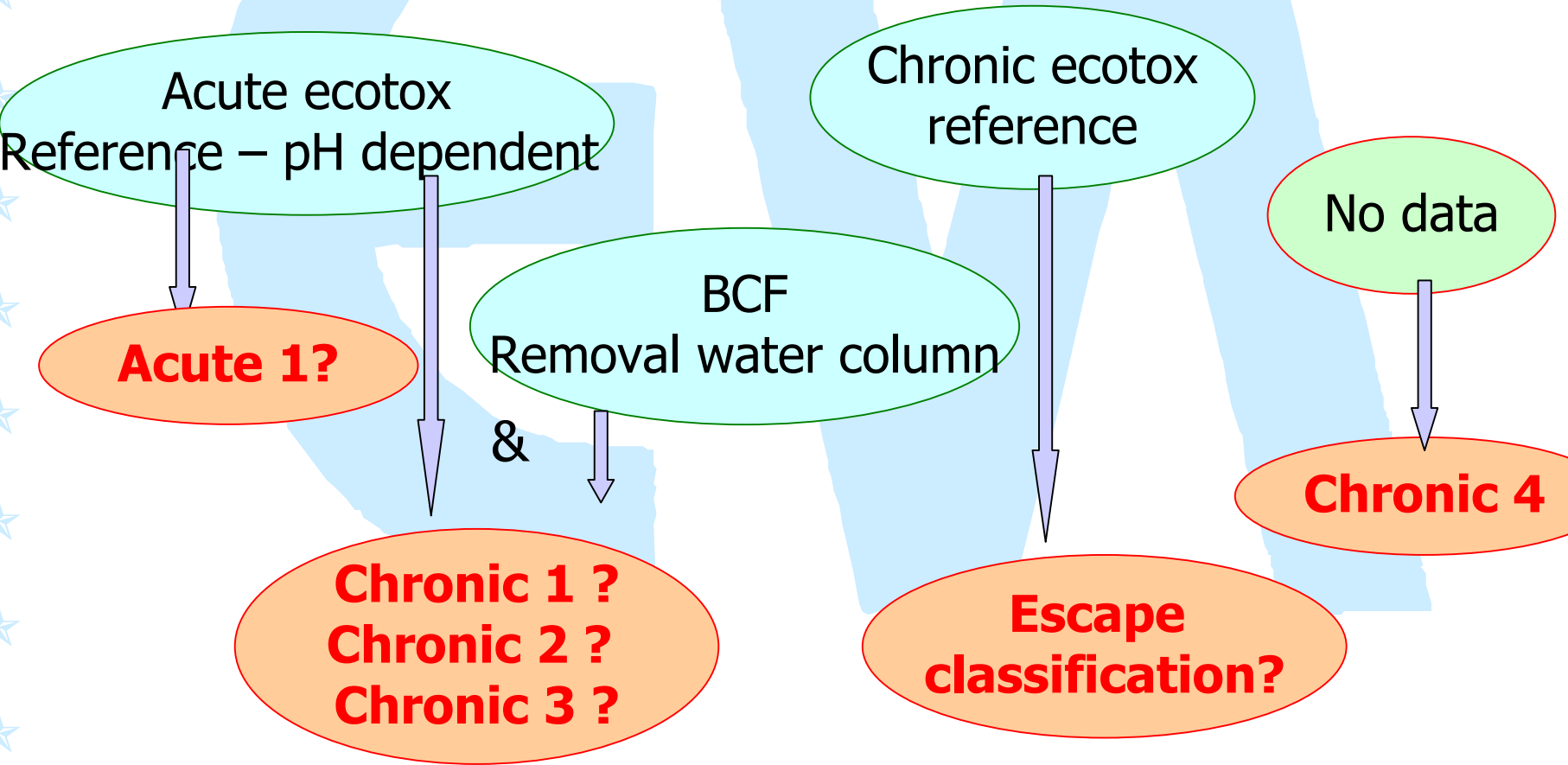
Chronic Escape clause

→ Removal of classification if
reference chronic NOEC > 1 mg/L

Summary

The CLP REGULATION : 1272/2008

= applicable to metals



EU Environmental Classification

→ **CLP REGULATION : 1272/2008**

RIP 3.6 to be finalized

To come

New OECD guidelines on chronic toxicity